

THE ANALYSIS OF COAL WITH THE LASER-MASS SPECTROMETER

by

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INTRODUCTION

The laser-mass spectrometer has been used to pyrolyse petrographic constituents of coal and record the mass spectrum of the pyrolysis products thus produced. The laser-mass spectrometer has been described in detail elsewhere (1,2). Essentially it consists of a small pulsed ruby laser (max. output energy 0.1 joule) whose output can be focused on the surface of a coal target located in the ionization chamber of a time-of-flight mass spectrometer. A modified microscope optical system is used to focus the laser; irradiated targets can be as small as 10 microns in diameter. Since the target to be irradiated can be viewed through the same microscope system, selected areas of the coal sample can be pyrolysed. With the 10 micron diameter limit of the irradiation zone different petrographic constituents of a coal sample can be pyrolysed in-situ and their mass spectra recorded. These spectra can be used to study the chemical composition and structure of coal or even more simply can be used as "fingerprints" to differentiate between the various heterogeneous constituents of coal.

LASER HEATING

The energy from the laser that irradiates the coal sample is not great (~ 0.01 cal.). However, since the energy is delivered in a short pulse and the high coherency of the laser light enables it to be focused on a small area, flux densities of 10^6 cal./sec./cm.² can be established at the coal surface. These high flux densities result in extremely rapid heating rates.

It is difficult to assign a temperature to a laser pyrolysis. If one assumes that only the material vaporized was heated estimated temperatures would be about 50,000°C. This value would be decreased considerably if the heat of decomposition of the coal was taken into account. Another factor even more difficult to evaluate is the shielding of the coal surface from the laser radiation by the plume of decomposition products. The presence of high molecular weight products in the mass spectrum would seem to indicate that the bulk of the pyrolysed coal did not reach temperature much above 1000°C. The high flux output of the laser establishes large temperature gradients in the heated solid but the short pulse length restricts pyrolysis to that material in the immediate vicinity of the irradiated zone. This is demonstrated by the fact that a second laser heating of a target produces a mass spectrum characteristic of a char rather than the original material, however if the laser is fired at an area 100 microns removed from a pyrolysed crater the resulting spectrum is the same as an unheated coal.

OBTAINING THE SPECTRA

The pulse length of the laser depends upon the pumping energy, under the conditions used in this investigation a typical pulse length would be about 300 microseconds. Most of the pyrolysis of the coal sample will take place during the actual laser burst. However, pyrolysis products are still being evolved several milliseconds after the laser burst due to the finite cooling time of the coal. The TOF mass spectrometer is capable

of making mass analysis of the species in the ionization chamber at 50 to 100 microsecond intervals enabling several spectra to be recorded during the pyrolysis.

The intensity of the masses recorded decreases exponentially with time. The rate of decay is not the same for all masses. In general the higher masses have the longer time constant. The distribution of decay rates cannot be accounted for by the effect of mass on pumping speed of the mass spectrometer vacuum system. A more likely explanation of the variation in decay rates of the different species is that the pyrolysis product distribution changes as the temperature of the coal decreases. For this investigation a single spectrum was recorded representing the composition one millisecond after the start of the laser burst.

THE SPECTRA

Figure 1 shows spectra obtained under similar conditions of the vitrain component of coals of several ranks. The ionization potential for all the spectra was 25 volts. The spectrum above mass 100 is magnified for ease of presentation for both the semi-anthracite and the sub-bituminous coals. With just a cursory glance one can see how easily vitrinites can be separated by the "fingerprint" technique. The general appearance of the mass spectra give some indication of the structure of the material. In the high mass region of the sub-bituminous vitrinite spectrum there are many mass peaks of about equal intensity. This tends to indicate a complex mixture of hydroaromatics and alkyl substituted aromatics. The HVA bituminous vitrinite has a much more differentiated spectrum in this region indicating more organization of structure. The semi-anthracite has a very simple mass spectrum as would be expected for a low hydrogen content, highly condensed ring system.

Figure 2 shows some comparison spectra. The high degree of similarity is seen between two HVA bituminous vitrinites from different sources. This can be contrasted to the dissimilarity between the spectrum of vitrain in sample number 1 and that of the non-vitrinitic material within 100 microns of the vitrain band edge. Although the latter two spectra have many of the same masses, differentiation can be easily accomplished by comparing selected peak ratios.

Major mass peaks can be found in the HVA spectra for the alkyl substituted benzenes and naphthalenes but the mass distributions of the spectra can not be accounted for by a mixture of stable molecules. The spectra indicate the presence of thermally produced free radicals in the pyrolysis products.

The laser-mass spectrometer is capable of differentiating between microscopic heterogeneities in coal. In order to understand the structural basis of this differentiation the behaviour of known materials under these pyrolysis conditions will have to be studied.

ACKNOWLEDGEMENT

This work was supported by a grant from the National Science Foundation.

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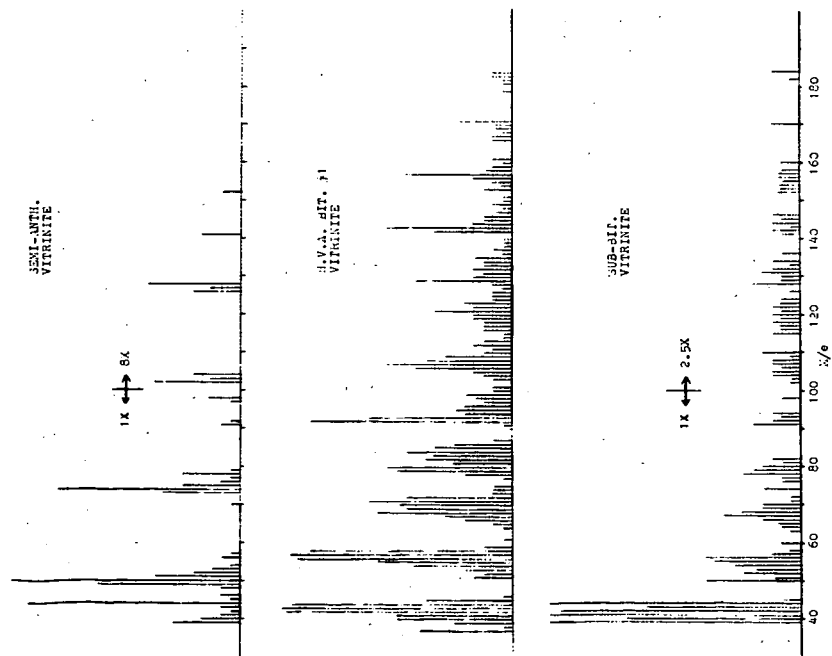


Figure 1: Mass spectra of vitrinites from selected coals.

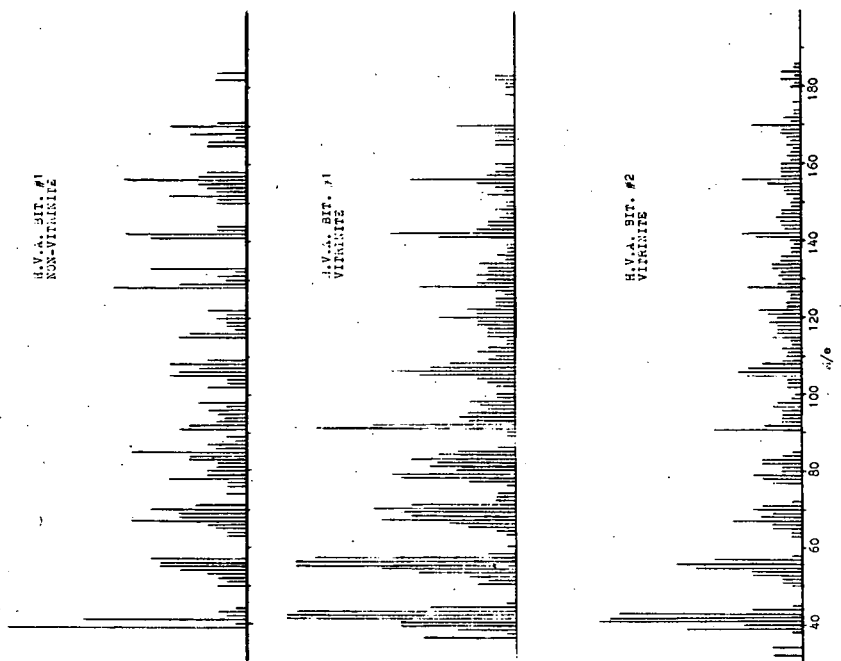


Figure 2: Mass spectra of selected components from h.v.a. bit. coals.